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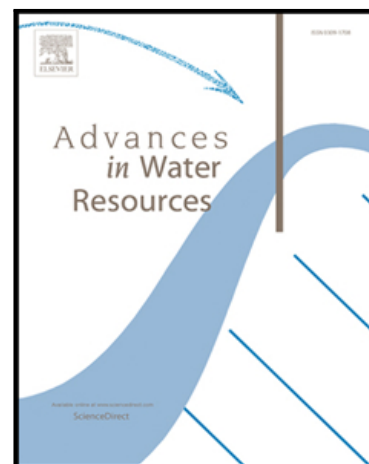
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## Highlights

- Imbibition and supercritical CO<sub>2</sub> dissolution experiments were conducted in four micromodels possessing different pore-scale characteristics.
- We present the fundamental process of the non-equilibrium CO<sub>2</sub> dissolution and coupling with water flow.
- We investigate the impacts of pore characteristics on the coupled processes.
- A diagram is proposed to quantify the equilibrium/non-equilibrium dissolution transition and network-dependent coupled processes.

# Coupled Supercritical CO<sub>2</sub> Dissolution and Water Flow in Pore-Scale Micromodels

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**Abstract:** Dissolution trapping is one of the most important mechanisms for geological carbon storage (GCS). Recent laboratory and field experiments have shown non-equilibrium dissolution of supercritical CO<sub>2</sub> (scCO<sub>2</sub>) and coupled scCO<sub>2</sub> dissolution and water flow, i.e., scCO<sub>2</sub> dissolution at local pores/pore throats creating new water-flow paths, which in turn enhance dissolution by increased advection and interfacial area. However, the impacts of pore-scale characteristics on these coupled processes have not been investigated. In this study, imbibition and dissolution experiments were conducted under 40 °C and 9 MPa using a homogeneous/isotropic hexagonal micromodel, two homogeneous elliptical micromodels with low or high anisotropy, and a heterogeneous sandstone-analog micromodel. The four micromodels, initially saturated with deionized (DI)-water, were drained by injecting scCO<sub>2</sub> to establish a stable scCO<sub>2</sub> saturation. DI water was then injected at different rates with  $\log C_a$  (the capillary number) ranging from -6.56 to -4.34. Results show that bypass of scCO<sub>2</sub> by displacing water is the dominant mechanism contributing to the residual CO<sub>2</sub> trapping, triggered by heterogeneity in pore characteristics or pore-scale scCO<sub>2</sub>-water distribution. Bypass can be enhanced by pore heterogeneity or reduced by increasing transverse permeability, resulting in relatively low (<2% of CO<sub>2</sub> solubility) or high (9 to 13% of CO<sub>2</sub> solubility) dissolved CO<sub>2</sub> concentration in displacing water. The overall dissolution of residual scCO<sub>2</sub> increases with decreasing  $C_a$ , and approaches to their solubility at low  $C_a$  value with sufficient residence time. This main trend is similar to a capillary desaturation curve that represents the relationship between the residual saturation and  $C_a$ . Spatially, dissolution initiates

along the boundary of bypassed scCO<sub>2</sub> cluster(s) in a non-equilibrium manner, and the coupling of water flow and dissolution occurs which fragments the bypassed scCO<sub>2</sub> clusters and enhance scCO<sub>2</sub> dissolution.

**Keywords:** Geological carbon storage, Micromodel, Pore characteristics, Imbibition, CO<sub>2</sub> dissolution, Mass transfer

## 1. Introduction

Accurate prediction of the long-term storage of CO<sub>2</sub> in subsurface formations depends largely on our understanding of involved processes, such as (1) two-phase fluid displacement and residual CO<sub>2</sub> saturation, and (2) dissolution of injected supercritical CO<sub>2</sub> (scCO<sub>2</sub>) and mass transfer of dissolved CO<sub>2</sub> (dsCO<sub>2</sub>) in formation brine (IPCC, 2005). The field tests of scCO<sub>2</sub> dissolution at the CO<sub>2</sub>CRC Otway site (Haese et al., 2013; Paterson et al., 2013) have shown unexpectedly early breakthrough and low maximum dsCO<sub>2</sub> concentrations (~30% of CO<sub>2</sub> solubility) in the produced water that were credited to formation heterogeneity, indicating the non-equilibrium scCO<sub>2</sub> dissolution and mass transfer at the field scale. At the core scale, Berg et al. (2013) conducted imbibition and scCO<sub>2</sub> dissolution experiments in a homogeneous high-permeability (380 mD) Berea sandstone core at 10 MPa and 45 °C by injecting dsCO<sub>2</sub>-undersaturated brine at 0.25 mL/min into the core after scCO<sub>2</sub> drainage. They observed strong dissolution of residual scCO<sub>2</sub> into displacing brine with relatively high dsCO<sub>2</sub> concentration (60% of CO<sub>2</sub> solubility). In contrast, Chang et al. (2013, 2014) observed that the complete, post-imbibition depletion of residual scCO<sub>2</sub> via dissolution was a prolonged process when injecting deionized (DI)-water free of dsCO<sub>2</sub> at 1.0 mL/min into two heterogeneous and low-permeability (<1 mD) sandstone cores at 8 MPa and 40 °C. The average dsCO<sub>2</sub> concentration was measured as 5% of CO<sub>2</sub> solubility, one order of magnitude lower than that in Berg et al. (2013). At the pore scale, Chang et al. (2016) investigated scCO<sub>2</sub> dissolution and mass transfer during imbibition in a heterogeneous sandstone-analog micromodel,

fabricated from section micrographs of a low-permeability Mt. Simon sandstone core (Zuo et al., 2013). Their time-lapse images of scCO<sub>2</sub>-water distributions provide direct observations of the non-equilibrium CO<sub>2</sub> dissolution and mass transfer, caused by bypass of residual scCO<sub>2</sub> by displacing water after imbibition, and slow mass transfer of dsCO<sub>2</sub> to displacing water. The inferred dsCO<sub>2</sub> concentrations in this centimeter-scale micromodel ranged from 0.38% to 2.72% of CO<sub>2</sub> solubility. The disparate observations in dsCO<sub>2</sub> concentrations across these scales indicate that the effects of formation heterogeneity and pore-scale characteristics on scCO<sub>2</sub> dissolution and mass transfer need to be investigated.

Laboratory experiments have also shown coupled scCO<sub>2</sub> dissolution and water flow, i.e., scCO<sub>2</sub> dissolution at local pores/pore throats creating new water-flow paths, which in turn enhance dissolution by increased advection and interfacial area. At the core scale, Akbarabadi and Piri (2013) observed an increase in brine relative permeability caused by gradual reduction in the blockage by trapped scCO<sub>2</sub> bubbles via dissolution. At the pore scale, Buchgraber et al. (2012) showed the disconnecting and shrinking of CO<sub>2</sub> bubbles due to dissolution, indicating scCO<sub>2</sub> snap-off and residual trapping. The disconnection and shrinkage of the CO<sub>2</sub> phase, in return, enhances CO<sub>2</sub> dissolution and mass transfer by increasing CO<sub>2</sub>-water interfacial area and creating new water-flow paths (Chang et al., 2016). Nambi and Powers (2000) and Zhang et al. (2002) reported similar coupled processes for the dissolution of non-aqueous phase liquid (NAPL) in water in heterogeneous sand boxes and columns packed with angular silica sands. Alternately, Chomsurin and Werth (2003) showed



constant NAPL dissolution rate with decreasing NAPL saturation during their imbibition experiments in 2D homogeneous and heterogeneous micromodels. Addressing the apparently contradictory observations requires a systematic study on the impacts of pore characteristics on trapping mechanism and dissolution of residual CO<sub>2</sub>.

When gravitational forces are negligible, the nature of two-phase displacement at the pore scale has been characterized by the dimensionless capillary number  $C_a$  that represents the relative effect of viscous forces versus capillary force, and by the viscosity ratio  $M$  between liquid phases. The  $C_a$  is often defined as follows,

$$C_a = (\mu \times \bar{u}) / (\sigma \times \cos\theta) \quad \text{Eq. (1)}$$

where  $\mu$  is the viscosity,  $\bar{u}$  the average Darcy velocity of the injected fluid,  $\sigma$  the interfacial tension, and  $\theta$  the contact angle between the injected and resident fluid (Lenormand, et al., 1988). The phase entrapment at a given  $C_a$  and  $M$  can be described by the Capillary Desaturation Curve (CDC), which represents the relationship between the residual non-wetting saturation and  $C_a$  (Sahimi, 1993; Castro et al., 2015). The pore-scale CDC has been investigated in a micromodel with a statistically generated pore-size distribution (Castro et al., 2015). Their results suggest the dependence of CDC shape on the amount and size distribution of the residual phase. It has also been reported that the traditional  $C_a$  in Eq. (1) should be revised using the length scales corresponding to the size of non-wetting phase clusters, and the revised  $C_a$  is referred to as cluster-based  $C_a$  (Hilfer and Oren, 1996; Armstrong et al., 2014). The influence of pore characteristics on pore-scale CDC and

cluster-based  $C_a$  for residual trapping and the later dissolution of residual  $\text{CO}_2$  needs further investigations.

In this study, we (1) present the fundamental trapping mechanism and the processes of the non-equilibrium  $\text{CO}_2$  dissolution coupled with water flow, (2) investigate the impacts of pore characteristics on  $\text{CO}_2$  trapping, the pore-scale CDC and the coupled processes, and (3) propose a diagram to quantify the network-dependent coupled processes. A series of imbibition and  $\text{scCO}_2$  dissolution experiments was systematically conducted in four micromodels with post-drainage  $\text{scCO}_2$  saturations by injecting  $\text{dsCO}_2$ -free brine at different rates. Time-lapse high-resolution images of  $\text{scCO}_2$  and water were obtained to provide direct observations of the coupled processes at the pore scale and to allow for comparisons among the different micromodels and with previous studies at the pore and core scales. The four micromodels represent typical pore characteristics of porous media with contrasts between homogeneity and heterogeneity, between isotropy and weak and strong anisotropy, and between different pore shapes.

We first present the details on the micromodels and experimental procedures in Section 2. We show in Section 3 the fundamental processes of  $\text{CO}_2$  dissolution coupled with water flow in a homogeneous isotropic micromodel at two low injection rates ( $\log C_a = -6.53$  and  $-6.13$ ), and then the effects of displacement rate on  $\text{CO}_2$  dissolution. In Section 4, we discuss the impacts of pore characteristics on the coupled processes by comparing the experimental observations in all the four micromodels. In Section 5, we present the pore-scale CDC and cluster-based  $C_a$  in different

micromodels. In Section 6, we propose a diagram to describe the network-dependent coupled processes and the overall trend between  $\text{dsCO}_2$  concentration and  $C_a$  or water residence time. We conclude our observations and include implications on field GCS in Section 7.

## 2. Materials and methods

### 2.1 Micromodels

Figure 1 shows the pore characteristics of the four micromodels used in this study, with pore space shown in white and silicon posts (representing mineral grains) in black. Micromodels were composed of etched silicon wafers fabricated using micro-fabrication methods involving standard photolithography, coupled plasma-deep reactive ion etching (ICP-DRIE), thermal oxidation, and anodic bonding (Chomsurin and Werth, 2003; Willingham et al., 2008). Micromodel #1 consists of hexagonal posts and a homogeneous isotropic pore network, with circular pore bodies (60  $\mu\text{m}$  in diameter), each connected with six pore throats (5  $\mu\text{m}$  in width). Micromodels #2 and #3 are homogeneous anisotropic micromodels, share the same elliptical silicon posts, and have different post arrangements and thus different longitudinal ( $k_l$ ) and transverse ( $k_t$ ) permeability. The ratio of  $k_t/k_l$  is calculated as 0.63 for Micromodel #2 and 6.86 for Micromodel #3, using the relation  $k = \frac{1}{2} \left( \frac{A}{P} \right)^2$ , where  $A$  and  $P$  represent the area and perimeter of a rectangular cross section, respectively (White, 1979). The design pore depth of the three micromodels is 37  $\mu\text{m}$ . The pore network of Micromodel #4 is extracted from a section micrograph of a Mt. Simon sandstone core

collected from the injection well of the Illinois Basin-Decatur project (Zuo et al., 2013; Senel et al., 2014). The porous medium portion consists of nine identical sub-images in a 3×3 array (see the red lines in Figure 1) and features in three lateral high-permeability channels (see Figure S1 in the supplementary information). A Local Thickness plugin in ImageJ software (Hildebrand and Rüesgsegger, 1996; Rasband, 1997-2018) was used to quantify the pore-size distribution shown in Figure S1. The average pore-body diameter and pore-throat width is 33 and 14  $\mu\text{m}$ , respectively. Figure S1 presents an example of the micromodel design including the pore network (#4) and the boundary conditions (Zuo et al., 2013). The triangle sections on each side of the pore allow for an uniform water displacement before entering the pore network (see Figure S3), reducing water film flow before invading the pore network. The inlet triangle volume was included when calculating the water injection pore volume (PV). Additional details on the pore-size distribution can be obtained from Chang et al. (2016). Table 1 lists the properties of the four micromodels used in this study.

## **2.2 Experiments and fluorescence imaging**

An experimental setup with four high-pressure syringe pumps (Teledyne ISCO Inc., Lincoln, NE) was used for all imbibition/dissolution experiments. The experimental setup is described in detail in the supplementary figure (Figure S2). Each micromodel was assembled against a sapphire viewing window in a high-pressure cell allowing imaging. The micromodel was initially saturated with deionized (DI)-water, and then drained by injecting Coumarin-dyed  $\text{scCO}_2$  (Biswas et

al., 1999) at a constant rate until stable scCO<sub>2</sub> distribution and saturation were established. The displaced water during drainage was collected in a pressure pump maintaining back-pressure at a constant fluid pressure of 9.00 MPa. After scCO<sub>2</sub> distribution and saturation remained stable with time, the scCO<sub>2</sub> distribution was imaged to calculate the baseline scCO<sub>2</sub> saturation. The same drainage procedure was repeated before each imbibition/dissolution experiment to obtain similar initial scCO<sub>2</sub> saturation ( $S_{g,i}$ ) and distribution.

Imbibition/dissolution experiments were conducted by injecting DI water at a constant volumetric rate until scCO<sub>2</sub> in the pore network was completely depleted. Displaced scCO<sub>2</sub> was collected in the back-pressure pump constantly maintained at 9.00 MPa. Different water injection rates were used for each micromodel (see Table 2). To allow for comparisons between imbibition/dissolution experiments and micromodels, we calculated the capillary number ( $C_a$ ) for each test from Eq. (1). The reported contact angle of water–Courmarin dyed scCO<sub>2</sub> in micromodels fabricated using similar silicon wafers is approximately 15° (Wang et al., 2012).  $\sigma$  is inferred from Chiquet et al. (2007) for scCO<sub>2</sub> and water.

During each imbibition/dissolution experiment, the stained scCO<sub>2</sub> in the micromodel was observed through a Blue GFP filter set ( $\lambda_{\text{ex}} = 379\text{-}401$  nm,  $\lambda_{\text{em}} = 435\text{-}485$  nm). Time-lapse images were obtained using a Nikon Eclipse TE2000-E epifluorescent inverted microscope (Melville, NY) equipped with a monochrome CCD camera (MU1003, AmScope) through a 4X objective with a spatial resolution of 1.62  $\mu\text{m}/\text{pixel}$ . During the experiment, images were taken at 2-40 min intervals,

depending on the water injection rates and durations. The fluorescent signal intensity of dyed scCO<sub>2</sub> is significantly higher than that for silicon posts and pore spaces filled with water, with signal-to-noise ratio > 10. A threshold value was unambiguously determined for each image to distinguish the scCO<sub>2</sub> phase from others following methods outlined by Zhang et al. (2011) and Chang et al. (2016). Segmentation and analysis of these images were conducted using ImageJ software (Rasband, 1997-2018). The image segmentation method was validated by comparing (1) the measured porosity from fluorescent images to that computed from the micromodel design and (2) the measured size of silicon posts to the design value. Both of the comparisons showed good agreement with errors <5%. For Micromodel #3, images taken at a resolution of 1.62  $\mu\text{m}/\text{pixel}$  failed to capture the very tight pore throat with 3  $\mu\text{m}$  width (see Figure 1), leading to an error in image segmentation and underestimation of the pore volume by <2.5%. CO<sub>2</sub> distributions were assumed to be uniform along the micromodel depth for the calculation of CO<sub>2</sub> saturations. This assumption has been widely used for 2D micromodel experiments (Zhang et al., 2011; Wang et al., 2013; Chang et al., 2017; Hu et al., 2017).

### **3. CO<sub>2</sub> imbibition and dissolution processes**

A series of imbibition/dissolution experiments was conducted in the homogeneous and isotropic Micromodel #1 under different displacement rates varying from 10 to 200  $\mu\text{L}/\text{h}$  ( $\log C_a = -6.53$  to  $-5.23$ ). During each experiment, time-lapse images of scCO<sub>2</sub> distribution were obtained to calculate a scCO<sub>2</sub> saturation and depletion rate ( $Q_d$ ).

### 3.1 Imbibition and residual CO<sub>2</sub> saturation

Figure 2a shows selected time-lapse images of scCO<sub>2</sub> distribution (green) obtained during the imbibition/dissolution experiment with  $\log C_a = -6.53$ . Water (dark) invades the pore network in several narrow (with 1-2 pore bodies wide) and long flow paths, and flows through the pore network within 2 min. Initially, the residual water clusters near the inlet help induce channelized water flow (see the white arrows at 0 and 5.6 PV in Figure 2a). The channelized water flow results in a high residual scCO<sub>2</sub> saturation ( $S_{g,r}$ ) of 0.82 (see Figure 2a at 6.4 PV injection and Table 3), with the majority of injected water flowing through water-flow channels and bypassing the rest of the pore network. Similar channelized water flow is observed in the imbibition/dissolution experiment with  $\log C_a = -6.13$  (see Figure 2b). Five narrow water-flow paths (at 1-2 pore width), labeled as C1, C2, C3, C4 and C5, have been created by 2.4 PV (22 min) after the start of water injection. The residual CO<sub>2</sub> saturation at the end of imbibition, when no additional CO<sub>2</sub> was displaced from the pore-network, is 0.79 (also see Table 3).

In this homogeneous micromodel, the bypass of scCO<sub>2</sub> by displacing water can be attributed to the initially heterogeneous fluid distribution near the inlet. Similar bypass trapping of residual CO<sub>2</sub> has been observed in a homogeneous micromodel (Hu et al., 2017) and a glass beads column (Chaudhary et al., 2013). At  $C_a > 10^{-7}$ , the main trapping mechanism was shown by the propagation of invading fluid fingers that lead to clusters of defending fluid being bypassed (Hu et al., 2017).

### 3.2 Coupled CO<sub>2</sub> dissolution and water flow

After imbibition, scCO<sub>2</sub> dissolution and mass transfer are dominant mechanisms for scCO<sub>2</sub> depletion with time. In the case with  $\log C_a = -6.53$ , a low-tortuosity flow path connected to the outlet gradually develops as the main water-flow path, and its width continuously increases with scCO<sub>2</sub> dissolution until the complete depletion of residual scCO<sub>2</sub> (see Figure 2a). Figures 3a-b show the temporal CO<sub>2</sub> saturation averaged over the pore network and effluent dsCO<sub>2</sub> concentration at the micromodel outlet as a function of water injection time or pore volume (PV) during the experiment, while Figure 3c shows the dependence of scCO<sub>2</sub> depletion rate (g/PV) on scCO<sub>2</sub> saturation. The rate of scCO<sub>2</sub> depletion is defined as the depleted scCO<sub>2</sub> mass (g) per PV and calculated from two consecutive images. The dsCO<sub>2</sub> concentration is calculated as follows on the basis of mass balance assuming that dissolution and water advection are solely responsible for the scCO<sub>2</sub> depletion after the imbibition is complete:

$$C = \frac{\rho P(S_{t2} - S_{t1})}{MQ(t_2 - t_1)} \quad \text{Eq. (2)}$$

Here  $C$  is the dissolved CO<sub>2</sub> concentration (mol/L),  $\rho$  is CO<sub>2</sub> density under experimental conditions (g/mL),  $P$  is pore volume of the porous network (mL),  $S_{t2}$  and  $S_{t1}$  indicates CO<sub>2</sub> saturation at two sequential images,  $t$  represents water injection time (min),  $Q$  is the water injection rate (L/min) and  $M$  (44 g/mol) refers to the CO<sub>2</sub> molar mass. Note that scCO<sub>2</sub> saturation, dsCO<sub>2</sub> concentration, and scCO<sub>2</sub> depletion rate are average values over the entire pore-network domain, if not otherwise specified. The assumption that dissolution and water advection are solely responsible for the scCO<sub>2</sub> depletion after the imbibition is made carefully by



substantial evidence showing no displacement of CO<sub>2</sub> occur after the completion of imbibition, i.e., the CO<sub>2</sub> bubbles/clusters at the outlet triangle void shrink due to dissolution and no additional CO<sub>2</sub> displaced out from the pore-network was seen (see Figure S3). The evaporation of water in scCO<sub>2</sub> was negligible when calculating the CO<sub>2</sub> depletion. Under the experimental conditions (40 °C, 9 MPa), the solubility of water in scCO<sub>2</sub> is  $\sim 3.5 \times 10^{-3}$  (mole fraction), while the solubility of scCO<sub>2</sub> dissolved in water is  $22 \times 10^{-3}$  in mole fraction (Spycher and Pruess, 2003). Meanwhile, the dissolution and mass transfer of scCO<sub>2</sub> in water are enhanced by water advection, while evaporation of water in scCO<sub>2</sub> is diffusion dominated in the stagnant CO<sub>2</sub>. Evaporation of water in scCO<sub>2</sub> thus has a limited effect on the scCO<sub>2</sub> depletion rate after imbibition.

As shown in Figure 3a, it takes 2,010 min to complete the depletion of scCO<sub>2</sub> by imbibition (150 min or 6 PV) and dissolution (1,860 min or 80 PV). The rate of scCO<sub>2</sub> depletion by dissolution (with initial scCO<sub>2</sub> saturation of 0.82) varies from  $1.67 \times 10^{-6}$  to  $4.72 \times 10^{-5}$  g/PV, and corresponds to an effluent dsCO<sub>2</sub> concentration of 0.82-22.4% of CO<sub>2</sub> solubility ( $C_s = 1.225$  mol/L) under the experimental conditions (Spycher and Pruess, 2003). In contrast, under equilibrium dissolution assumption, 6.7 PV of injected water is needed to completely dissolve the residual CO<sub>2</sub> in the pore network, corresponding to 97 min at the 10  $\mu$ L/h (0.069 PV/min) water injection rate.

The coupled scCO<sub>2</sub> dissolution and water flow can be first understood by the non-monotonic temporal change in scCO<sub>2</sub> depletion rate, i.e., scCO<sub>2</sub> depletion rate increases first from  $0.2 \times 10^{-5}$  g/PV to  $4.7 \times 10^{-5}$  g/PV first with decreasing scCO<sub>2</sub>

saturation in the pore network from 0.80 until a certain value (0.45 in Figure 3c), after which the rate decreases. This trend is also seen in Figure 3b for  $dsCO_2$  concentration. To improve understanding of the coupled processes, we depict in Figure 4 the fraction and location of  $scCO_2$  mass dissolved within different time intervals in the micromodel at  $\log C_a = -6.53$ , with different colors corresponding to different injection times and PVs. Along the boundary layers (marked by white dotted lines) of the two bypassed  $scCO_2$  clusters separated by the single water-flow path, water flow develops in local pores/pore clusters and breaks large connected  $scCO_2$  clusters by dissolution (see the white arrows – cooler colors in warmer color regions). The local water-flow paths developed by  $scCO_2$  dissolution greatly increase the average  $dsCO_2$  concentration in the entire pore network from 0.82% to 22.4% of  $CO_2$  solubility. The increased  $scCO_2$  dissolution rate by coupled dissolution and water flow is similar to that observed experimentally by Zhang et al. (2002) and Chang et al. (2016) and verified numerically by Zhao et al. (2003). At later times, this coupling of  $scCO_2$  dissolution and water flow is weakened due to the reduced residual  $CO_2$  mass available for dissolution. The overall  $dsCO_2$  concentration vs. water injection volume and  $CO_2$  depletion rate vs.  $CO_2$  saturation thus shows a maximum value.

The coupling between  $scCO_2$  dissolution and water flow can be further understood by the multiple water-flow paths and their competition in the case with  $\log C_a = -6.13$ . As shown in Figure 2b, flow paths #C2, #C3 and #C4 increases in their width simultaneously during the first 214 min. After that, all injected water migrates through flow path #C2 and its width increases with time until the complete depletion of

residual scCO<sub>2</sub>. Figure 5a-c shows magnified local regions with 30 pores wide along each flow path to show the competition between flow paths #C2 through #C4, and in Figure 5d shows the temporal saturation change during the first 244 min (17 PV). For #C2, upstream scCO<sub>2</sub> dissolves into the displacing water along the flow path, and scCO<sub>2</sub> saturation decreases almost linearly with time from 0.81 to 0.74, indicating a relatively constant scCO<sub>2</sub> dissolution rate. Along #C3, however, scCO<sub>2</sub> saturation decreases nonlinearly with time from 0.72 to 0.68 with a decreasing CO<sub>2</sub> dissolution rate. The stable scCO<sub>2</sub> bubbles within the narrow flow path (marked by the red arrow in Figure 5b) may indicate high, local dsCO<sub>2</sub> concentration close to solubility. In #C4, as scCO<sub>2</sub> dissolves in the upstream water, a large scCO<sub>2</sub> cluster is displaced and blocked the narrow flow path downstream. This local displacement terminates the water flow and reduces CO<sub>2</sub> depletion rate. After 214 min, #C3 and #C4 are suppressed, and #C2 dominates further scCO<sub>2</sub> depletion in the entire pore network (see Figure 2b). For #C1 and #C5, the water flow paths are not connected to the micromodel outlet after imbibition, resulting in a constant CO<sub>2</sub> saturation as shown in Figure 5d.

Figures 3d and e show the temporal network-averaged CO<sub>2</sub> saturation and effluent dsCO<sub>2</sub> concentration as functions of water injection time or volume for the case with  $\log C_a = -6.13$ , while Figure 3f shows the dependence of scCO<sub>2</sub> depletion rate on scCO<sub>2</sub> saturation. The scCO<sub>2</sub> depletion rate increases from  $4.0 \times 10^{-6}$  to  $1.9 \times 10^{-5}$  g/PV and the corresponding dsCO<sub>2</sub> concentration varies from 1.88 to 8.98% of CO<sub>2</sub> solubility. Figure 6 depicts the fraction and location of scCO<sub>2</sub> mass dissolved at

different injection times and volumes, indicating that the coupled scCO<sub>2</sub> dissolution and water flow occur in the boundary layers of bypassed scCO<sub>2</sub> clusters. As shown in the figure, the main water flow path (C2) is less tortuous than that in Figure 4, and the coupled water flow and dissolution is less pronounced with reduced transverse water flow into the bypassed scCO<sub>2</sub> clusters.

An additional imbibition experiment without dissolution was conducted by injecting dsCO<sub>2</sub>-saturated water at  $\log C_a = -6.13$ . Figure 7 shows the time-lapse images and tortuous water-flow paths. The residual scCO<sub>2</sub> saturation after imbibition (without dissolution) is 0.72. The tortuous flow paths are compared to the five straight ones in Figure 2b. This indicates that dissolution can lead to scCO<sub>2</sub> displacement in more focused, less tortuous, narrower flow paths with reduced sweep efficiency. The depletion of scCO<sub>2</sub> by dissolution at local pores may enhance water flow development and reduce resistance from scCO<sub>2</sub> within the flow path. Similar observations have been presented by Chang et al. (2016).

### 3.3 Effects of water velocity on imbibition and dissolution

The velocity effects on imbibition and dissolution were investigated by increasing water injection rates in the imbibition/dissolution experiments conducted in Micromodel #1. Figure 8 shows the time-lapse images of scCO<sub>2</sub>-water distribution in the cases with  $\log C_a = -5.83$ ,  $-5.53$  and  $-5.23$ . Injected water displaces scCO<sub>2</sub> in randomly distributed forward and lateral flow paths (i.e., in the form of a dendritic front), leaving small scCO<sub>2</sub> clusters entrapped. Sweep efficiency is greatly increased with increasing displacement rates, resulting in larger number and width of the

invading water flow paths, resulting in residual  $\text{scCO}_2$  saturation (at the end of imbibition) at 0.57, 0.58 and 0.47 for  $\log C_a = -5.83$ ,  $-5.53$  and  $-5.23$ , respectively (see Table 3). The imbibition characteristics appears to transit from channelized water flow observed in the two low flow rate cases with  $\log C_a = -6.53$  and  $-6.13$  to dendritic displacement in the higher-rate cases.

The transition of water-flow regimes (from channeling flow to dendritic displacement) shown in Figures 2 and 8 may also be attributed to the high pore-throat aspect ratio (12) of Micromodel #1 and increased viscous force with injection rates. This transition observed experimentally in this study is similar to that obtained by pore-scale modeling with different flow rates and pore-throat aspect ratios conducted by Hughes and Blunt (2000). They found channelized water flow in the case with a small water injection rate ( $\log C_a = -6.0$ ) and a high pore-throat aspect ratio (3.95) and dendritic displacement in the cases with higher injection rates ( $\log C_a > -6.0$ ) and both high and low pore-throat aspect ratio (3.95 and 2.1).

The rate-dependent imbibition characteristics considerably impact the subsequent  $\text{scCO}_2$  dissolution and mass transfer. Figure 9 shows the depletion of the residual  $\text{scCO}_2$  by dissolution at different time and water injection volumes for the three high-rate experiments. After imbibition, small isolated  $\text{scCO}_2$  clusters within the water-flow paths dissolve first, followed by the larger bypassed clusters. The coupled dissolution and local water flow (marked by the white arrows in Figure 9) occur and enhance  $\text{scCO}_2$  dissolution in the pore network. Figure 10 shows the comparison of the time-dependent  $\text{scCO}_2$  saturation,  $\text{dsCO}_2$  concentration, and  $\text{scCO}_2$  depletion rate

among the five experiments with  $\log C_a$  from  $-6.53$  to  $-5.23$  conducted in Micromodel #1. The  $\text{scCO}_2$  depletion time after imbibition is 1860, 1272, 557, 235, and 122 min, respectively (see Table 3), indicating the effect of flow rate on the  $\text{scCO}_2$  residual saturation and the enhanced dissolution with flow rate. In contrast, it would take 97, 40, 14, 7 and 3 min for equilibrium dissolution to completely deplete residual  $\text{scCO}_2$  in the corresponding experiment. The prolonged depletion time indicates non-equilibrium  $\text{dsCO}_2$  dissolution in the homogeneous pore network caused by (1) non-uniform  $\text{scCO}_2$ -water distribution after imbibition and (2) non-uniform water-flow paths during dissolution. The depletion time mainly depends on the dissolution rate of large  $\text{scCO}_2$  clusters surrounded by water-carrying flow paths, even though enhanced dissolution can be caused by additional, local or global, water-flow paths.

Figure 10b displays that the peak  $\text{dsCO}_2$  concentration (caused by coupled dissolution and water flow) decreases with increasing imbibition rates (larger  $C_a$ ). These rate-dependent coupled processes can be attributed to the residence time of injected water in the pore network. Longer residence time with lower imbibition rates allows for longer contact between  $\text{scCO}_2$  and mobile water that is available for dissolution and mass transfer. In addition, because of the water-wet silica surface, water flow may occur as thin film along the surface of the silica posts (Zhao et al., 2016; Zacharoudiou et al., 2017; Hu et al., 2018). The swelling of water films was investigated as a slow diffusion process driven by capillary pressure at localities (Nguyen et al., 2006), i.e., with the increase in water injection rate, the time for

swelling of wetting films and development of local water flow is shortened. The coupling between dissolution and local water flow is thus limited, reducing the  $\text{scCO}_2$  concentration in the pore network. This indicates that water flow at a high velocity is less effective in dissolving residual  $\text{scCO}_2$  than that at a slower velocity and equilibrium  $\text{scCO}_2$  dissolution may only occur in regional groundwater flow with a very small (close to zero) velocity (to be further discussed in Section 5).

#### **4. Effects of pore characteristics**

Imbibition and dissolution experiments were conducted in Micromodels #2, #3 and #4 to improve understanding of the impacts of pore characteristics (i.e., anisotropy and heterogeneity) on  $\text{CO}_2$  dissolution and its coupling with water flow.

##### **4.1 Anisotropy with higher longitudinal permeability, $k_t/k_l=0.63$**

In Micromodel #2 with higher longitudinal permeability ( $k_t/k_l=0.63$ ), two imbibition and dissolution experiments were conducted by injecting water at 10 and 50  $\mu\text{L/h}$  ( $\log C_a = -6.56$  and  $-5.86$ ). Due to the higher longitudinal permeability, both drainage and imbibition efficiencies are reduced compared to Micromodel #1. After drainage,  $\text{scCO}_2$  saturations are  $\sim 0.50$  for subsequent imbibition experiments. Figures 11a and b show selected temporal images of  $\text{scCO}_2$ -water distribution during the two experiments. Water invades the pore network from left boundary in narrow flow channels (marked by white dotted lines) with reduced displacement efficiency, leading to residual  $\text{scCO}_2$  saturation of 0.43 and 0.44 after imbibition.

Figure 11c-e show the temporal CO<sub>2</sub> saturation, dsCO<sub>2</sub> concentration, and scCO<sub>2</sub> depletion rate. The residual CO<sub>2</sub> was completely depleted after water injections at 1300 and 275 min, corresponding to 55 and 60 PV (see Figure S4a), respectively, with  $\log C_a = -6.56$  and  $-5.86$ . The CO<sub>2</sub> depletion rate increases with decreasing scCO<sub>2</sub> saturation (Figure 11e) and the dsCO<sub>2</sub> concentration increases with water injection volumes (Figure 11d), indicating the coupling of CO<sub>2</sub> dissolution with water flow. The coupling occurs when water-flow paths merge with stagnant water clusters (see the white arrows in Figure 11a) and several flow paths merge into a large one (see the white arrows in Figure 11b).

#### 4.2 Anisotropy with higher transverse permeability, $k_t/k_l = 6.86$

Two imbibition/dissolution experiments were conducted in Micromodel #3 with a higher transverse permeability ( $k_t/k_l = 6.86$ ) by injecting water at 10 and 50  $\mu\text{L/h}$  ( $\log C_a = -6.27$  and  $-5.58$ ). Under these conditions, both drainage and imbibition efficiency is high compared to Micromodels #1 and #2. scCO<sub>2</sub> saturation is stable at  $\sim 0.90$  after drainage and injected water invades widely, distributed over the entire pore network (see Figure 12a and b). The displaced CO<sub>2</sub> saturation is 0.38 and 0.49, respectively, resulting in residual CO<sub>2</sub> saturation at 0.52 and 0.44 after imbibition (see Table 3).

The temporal change in CO<sub>2</sub> saturation is shown in Figure 12c. It takes 320 min (19 PV) and 90 min (27 PV) to completely deplete the scCO<sub>2</sub> by imbibition and dissolution at  $\log C_a = -6.27$  and  $-5.58$ , respectively (see Figure S4b for the change of CO<sub>2</sub> saturation vs. injected water pore volumes). The depletion of residual scCO<sub>2</sub>



by dissolution starts after 40 min (5 PV) and 20 min (13 PV) and the  $dsCO_2$  concentration monotonically decreases with increased water injection volumes (see Figure 12d). A monotonic decrease is also observed for the temporal change in  $CO_2$  depletion rate (Figure 12e). The fast depletion and high  $dsCO_2$  concentration by dissolution in these two experiments can be attributed to the strong water-film flow driven by high capillary pressure in the very tight pores and pore throats in Micromodel #3. The distributed contact between  $scCO_2$  and mobile water is pervasive through the entire pore network, promoting  $scCO_2$  dissolution everywhere. No dominant water-flow paths are observed.

### 4.3 Sandstone-analog heterogeneity

A series of imbibition and dissolution experiments were conducted in (heterogeneous sandstone-analog) Micromodel #4 and reported in Chang et al. (2016). Time-lapse images of  $scCO_2$ -water distribution show water preferential water flow along the high-permeability channels and bypass the majority of pore-network domain, where  $CO_2$  was trapped and residual water after drainage was stagnant (see Figure 13). The results of dynamic  $dsCO_2$  concentration vs. water injection show that  $scCO_2$  dissolution at the pore-network scale is controlled by (1) the number of water-flow paths developed along the high-permeability channels, and (2) the velocity of water flow or dissolution time. At a low injection rate ( $\log C_a = -5.34$ ), one water-flow path develops with strong coupling between dissolution and water flow. With increasing in water injection rate ( $\log C_a = -4.34$ ), 2-3 water-flow paths develop along the high-permeability channels, while the coupling between dissolution and water flow is

diminished and  $dsCO_2$  concentration decreases with water injection volumes. More details on the water flow and  $scCO_2$  dissolution can be seen in Figures S5 and S6 in the supporting material and Chang et al., (2016). In summary, the coupling of dissolution with water flow in this heterogeneous micromodel depends largely on injection rate and capillary number.

## 5. Pore-scale capillary desaturation curve and cluster-based capillary number

Figure 14 shows the residual  $scCO_2$  saturation and effluent  $dsCO_2$  concentration as a function of  $C_a$  for the 13 imbibition and dissolution experiments in the four micromodels. The evolution of pore-scale residual  $CO_2$  saturation follows a typical CDC for Micromodels #1 and #4, and the residual  $CO_2$  saturations remain high at low  $C_a$  and decrease sharply at a critical  $C_a$  (marked by the arrows in Figure 14a). The residual  $CO_2$  saturation in Micromodel #1 shows a reduction from 0.82 to 0.47, larger than that from 0.54 to 0.37 in Micromodel #4. Meanwhile, the residual  $CO_2$  saturation decreases considerably at  $\log C_a = -5.83$  in Micromodel #1, while a great reduction occurs at  $\log C_a = -5.34$  in Micromodel #4. This indicates a higher viscous force is required for mobilizing the trapped  $CO_2$  in the heterogeneous micromodel (#4). The pore heterogeneity tends to limit water flow in high-permeability channels and reduce viscous force to the bypassed  $CO_2$ . While the CDC for Micromodels #2 and #3 are not complete, residual  $CO_2$  saturations in the two anisotropic micromodels are lower than in Micromodels #1 and #4 at similar  $C_a$ , caused by a lower drainage efficiency in Micromodel #2 and a higher imbibition efficiency in Micromodel #3 (see Tables 2

and 3).

As shown in Figure 14b, the  $dsCO_2$  concentration generally decreases with increasing  $C_a$ , consistent with the CDC in Figure 13a. Under the same  $C_a$ , the  $dsCO_2$  concentration increases with increasing water displacement efficiency from the lowest (<2% of  $CO_2$  solubility) in Micromodel #4 to highest (9-13% of  $CO_2$  solubility) in Micromodel #3. The  $dsCO_2$  concentrations in Micromodels #1 and #2 range from 2 to 5% of  $CO_2$  solubility.

The CDC shown in Figure 14a represents the pore-network-scale sweep efficiency as channelized water flow and bypass dominate the displacement. The bypassed pore-network domain may be composed of both trapped  $CO_2$  ganglia and stagnant water (see Figure 13), which does not transfer viscous force or contribute to the mobilization of  $CO_2$ . Here, we calculate the cluster-based capillary number,  $\overline{C_a}$ , following Hilfer and Oren (1996):

$$\overline{C_a} = \frac{l^{cl} \mu \bar{u}}{k p_b} \quad \text{Eq. (3)}$$

where  $l^{cl}$  is the average cluster length with saturation-weighting for each cluster:

$$l^{cl} = \frac{\sum s_c l_{cl}}{\sum S_c} \quad \text{Eq. (4)}$$

$l_{cl}$  represents the cluster size of the bypassed pore-network domain, instead of individual  $CO_2$  ganglia from Hilfer and Oren (1996),  $k$  is the absolute brine permeability, and  $p_b$  is the capillary pressure at breakthrough, estimated from the pore size and depth of the micromodel:

$$p_b = \frac{\sigma \cos \theta (r_1 + r_2)}{r_1 r_2} \quad \text{Eq. (5)}$$

In Eq. (5),  $\sigma = 28 \text{ mN/m}^2$  (Chiquet et al., 2007), and for Micromodel #1,  $r_1 = 60 \text{ }\mu\text{m}$ ,  $r_2 = 37 \text{ }\mu\text{m}$ ; for Micromodel #2,  $r_1 = 106 \text{ }\mu\text{m}$ ,  $r_2 = 37 \text{ }\mu\text{m}$ ; For Micromodel #3,  $r_1 = 41.6 \text{ }\mu\text{m}$ ,  $r_2 = 37 \text{ }\mu\text{m}$ ; For Micromodel #3,  $r_1 = 33 \text{ }\mu\text{m}$ ,  $r_2 = 35 \text{ }\mu\text{m}$ . The  $l^{cl}$  values for each imbibition/dissolution experiment are listed in Table 3.

Figure 14c displays CDC with  $\overline{C_a}$ . The desaturation of  $\text{CO}_2$  occurs at  $\overline{C_a} = 0.52$  and 1.69 in Micromodels #1 and #2, respectively. If individual  $\text{CO}_2$  ganglia are used for calculating  $\overline{C_a}$ , the plot for Micromodel #4 shifts left by  $\sim 2$  orders of magnitude.  $\overline{C_a}$  may be modified further with measurements of relative permeability following Armstrong et al. (2014). We show here the uncertainty of determining the cluster size, and the important role of water flow regime. While the cluster-based capillary number provides new insights into the non-wetting phase mobilization when considering the system characteristics (both pore space and resident fluid), a broader application requires a better calculation of the size of the non-wetting phase clusters, especially when direct visualization and imaging are unavailable.

## 6. The relation between ds $\text{CO}_2$ concentration and $\log C_a$

We've shown in Sections 3 and 4 that the bypass of sc $\text{CO}_2$  by displacing water is the dominant mechanism contributing to residual  $\text{CO}_2$  trapping without buoyancy. Bypass can be caused by the heterogeneity of pore characteristics (e.g., Micromodel #4) and pore-scale fluid distribution after drainage (e.g., Micromodels #1, #2 and #3). After imbibition, dissolution of residual  $\text{CO}_2$  is dependent on the displacement rate and pore characteristics. In Figure 15a, we show the correlation of ds $\text{CO}_2$  concentration vs. Peclet number ( $Pe$ ) for the imbibition/dissolution experiments

conducted in the four micromodels. The overall  $\text{dsCO}_2$  concentrations decrease with increasing  $Pe$ , which can be attributed to (1) the decrease in residual  $\text{CO}_2$  saturation after imbibition for dissolution, (2) the decrease in residence time, and (3) the reduced coupling between  $\text{CO}_2$  dissolution and water flow. We also note the effects of pore characteristics on  $\text{CO}_2$  dissolution and mass transfer. For instance, under the same range of  $Pe$  (0.3 to 17),  $\text{dsCO}_2$  concentration is lowest in the heterogeneous micromodel because of the preferential water flow along the high-permeability channels (see Figure S5-6 for details). The value is highest in the strong anisotropic Micromodel #3 with higher transverse permeability ( $k_t/k_l=6.86$ ), and 2 to 5% of solubility in homogeneous Micromodel #1 and weakly anisotropic Micromodel #2. The change of  $\text{dsCO}_2$  concentration vs. Reynold number ( $Re$ ) shows a similar trend (see Figure 15b and Table 2 and 3).

To improve understanding of the  $\text{scCO}_2$  dissolution process for these experiments in particular, and other non-wetting phase fluids in general, we propose a diagram between the relative concentration of dissolved constituents and flow velocity in terms of  $\log C_a$ . The diagram (Figure 16) includes (1) the average  $\text{dsCO}_2$  concentration (solid symbol) and the range between maximum and minimum time-dependent concentrations (bar) in each dissolution experiment in this study, (2) the average and range of  $\text{dsCO}_2$  concentration obtained in the core-flooding tests conducted in two low-permeability sandstone cores (Chang et al., 2014), (3) the average concentration obtained in a high-permeability Berea sandstone core (Berg et al., 2013), and (4) dissolved NAPL concentrations obtained in dissolution

experiments conducted in homogeneous and heterogeneous micromodels with  $\log C_a = -6.80$  and  $-6.0$  (Chomsurin and Werth, 2003). The flow velocity, capillary number and Reynolds number in Berg et al. (2013) are 0.37 m/day,  $9.3 \times 10^{-8}$  and 1.06, while the values in Chang et al. (2014) are 0.73 m/day,  $1.8 \times 10^{-7}$  and 0.64. The relative concentration (in percentage) to the solubility of  $\text{scCO}_2$  or NAPL under the experiment conditions is used in the diagram.

The overall trend shown in Figure 16 is that the dissolved non-wetting phase fluid concentration increases with a decrease in  $\log C_a$  (i.e., the increase in water residence time), and approaches to their solubility with sufficient residence time. In addition to the main trend, the relative dissolved phase concentration is also affected by the pore heterogeneity and anisotropy, and the coupled dissolution and water flow that depend on limited or pervasive water-flow paths in the regime of non-equilibrium dissolution. This effect can be understood by the wide range of relative concentration for a given  $\log C_a$  or water residence time. The average relative concentration varies from the lowest (<2%) in Micromodel #4, with strong heterogeneity, to the highest (9 to 13%) in Micromodel #3, with strong anisotropy. In Micromodels #1 and #2, with isotropic homogeneity and weak anisotropy, the concentration ranges from 2 to 5%. The lower relative concentration in the heterogeneous micromodel implies that for the same groundwater velocity, it may take longer residence time (or water flow path length) in a heterogeneous formation for  $\text{scCO}_2$ -water to reach equilibrium dissolution than that in a homogeneous one. Through the  $\text{dsCO}_2$  concentration vs.  $\text{CO}_2$  saturation observed in the four micromodels (Figures 11, 12 and 13), we are able to classify (1) Zone I,

where relative concentration monotonically decreases with decreasing residual saturation (marked by the red bars) and no coupling of CO<sub>2</sub> dissolution and water flow was observed, and (2) Zone II, where relative concentration non-monotonically changes with decreasing residual CO<sub>2</sub> saturation (marked by the black bars) and dissolution is coupled with water flow. Zones I and II are divided at a relative concentration of 5% (the dashed line) and  $\log C_a$  of  $-5.20$ . The dashed line for 2% concentration separates the dsCO<sub>2</sub> concentration in the heterogeneous micromodel from the other micromodels and cores. The proposed diagram helps describe the conditions that the coupled dissolution and water flow may occur at both pore scale with varying pore characteristics and core scale with varying porosities and permeabilities.

## 7. Conclusions and implications

We've systematically investigated the non-equilibrium CO<sub>2</sub> dissolution and its coupling with global and local water flow using four micromodels that represent porous media with varying anisotropy, heterogeneity, and pore-throat aspect ratio. Time-lapse images of scCO<sub>2</sub>-water distributions were obtained during each imbibition and dissolution experiment to quantify the dynamic dissolution process.

In the four centimeter-scale micromodels and at imposed water velocities (resulting in  $\log C_a = -6.56$  to  $-4.34$ ), we show that bypass of scCO<sub>2</sub> by displacing water is the dominant mechanism contributing to residual CO<sub>2</sub> trapping without buoyancy. Bypass can be triggered by heterogeneity in pore characteristics (e.g., Micromodel #4) and pore-scale scCO<sub>2</sub>-water distribution (e.g., Micromodels #1 and

#2). Higher transverse permeability (e.g., Micromodel #3) may reduce the bypass and increase pore-network sweep efficiency. After imbibition, dissolution dominates the depletion of residual  $\text{CO}_2$ . We show the dissolved  $\text{CO}_2$  concentration increases with increasing water displacement efficiency under same rates from the lowest (<2% of  $\text{CO}_2$  solubility) in Micromodel #4 to highest (9 to 13% of  $\text{CO}_2$  solubility) in Micromodel #3. The low  $\text{dsCO}_2$  concentration in the heterogeneous micromodel implies that under the same groundwater velocity, it may take longer residence time (or water flow path length) in a heterogeneous formation for  $\text{scCO}_2$ -water to reach equilibrium dissolution than that in a homogeneous one.

The diagram between relative dissolved concentration and  $\log C_a$  was developed by using the average and range of relative concentrations in each of the 13 experiments and in published core and micromodel experiments. The diagram shows that the concentration of dissolved non-wetting phase fluids (e.g.,  $\text{dsCO}_2$ ) increases with the decreasing capillary number, and approaches solubility at low  $C_a$  value with sufficient residence time. This main trend is similar to a CDC in a bypass-dominated displacement. Spatially, dissolution of residual  $\text{CO}_2$  initiates along the boundary of the bypassed  $\text{CO}_2$  cluster(s) in a non-equilibrium manner, and the  $\text{dsCO}_2$  concentration in water decreases with increasing  $C_a$  and  $Pe$ . The main trend is secondarily affected by the coupled dissolution and water flow at localities that fragment the bypassed  $\text{scCO}_2$  clusters and enhance  $\text{scCO}_2$  dissolution at the pore scale.

For a reservoir-scale  $\text{scCO}_2$  plume after cessation of injection, residual  $\text{CO}_2$



trapping may be dominated by capillary snap-off as ambient groundwater flow rate is relatively slow ( $C_a < 10^{-7}$ ). The long residence time favors local dissolution and coupled with water flow to approach near equilibrium dissolution. On the other hand, due to the heterogeneous nature of reservoir formations, drainage and imbibition may focus flow in high-permeability channels, and fast dissolution of residual CO<sub>2</sub> into flowing water can be expected. For a scCO<sub>2</sub> plume in those low-permeability regions, dissolution is expected to be a lengthy process because of limited interfacial area between mobile water and immobile scCO<sub>2</sub>. Coupling of water flow and dissolution at localities may occur after the completion of main imbibition in the high-permeability channels, and shorten the dissolution process to some extent. In summary, the reservoir-scale dissolution will be collectively affected by slow ambient groundwater flow and strongly heterogeneity-controlled interfacial areas between groundwater flow and the scCO<sub>2</sub> plume.

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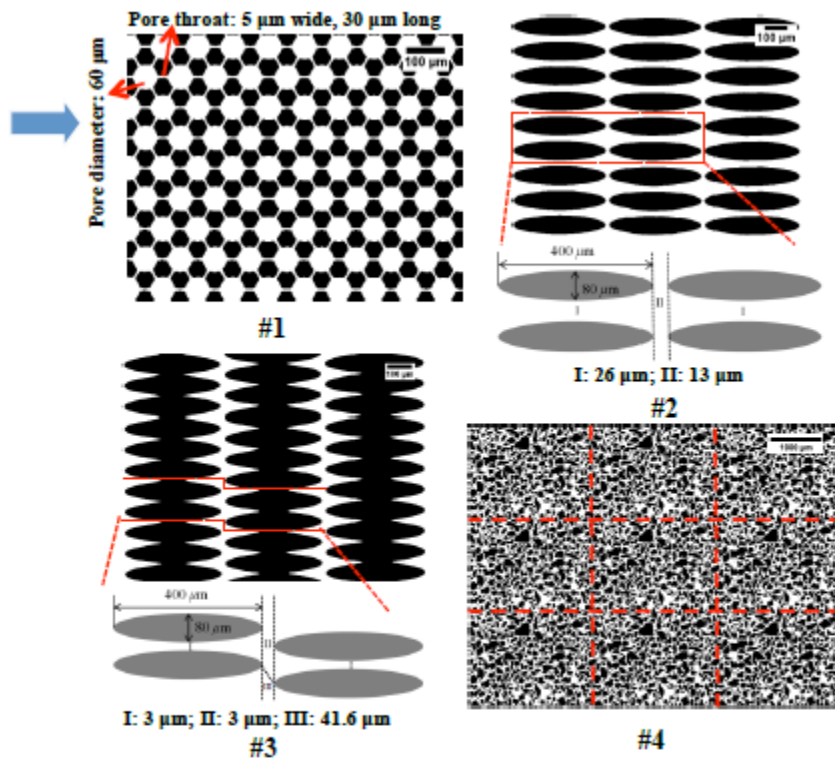
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## List of Figures

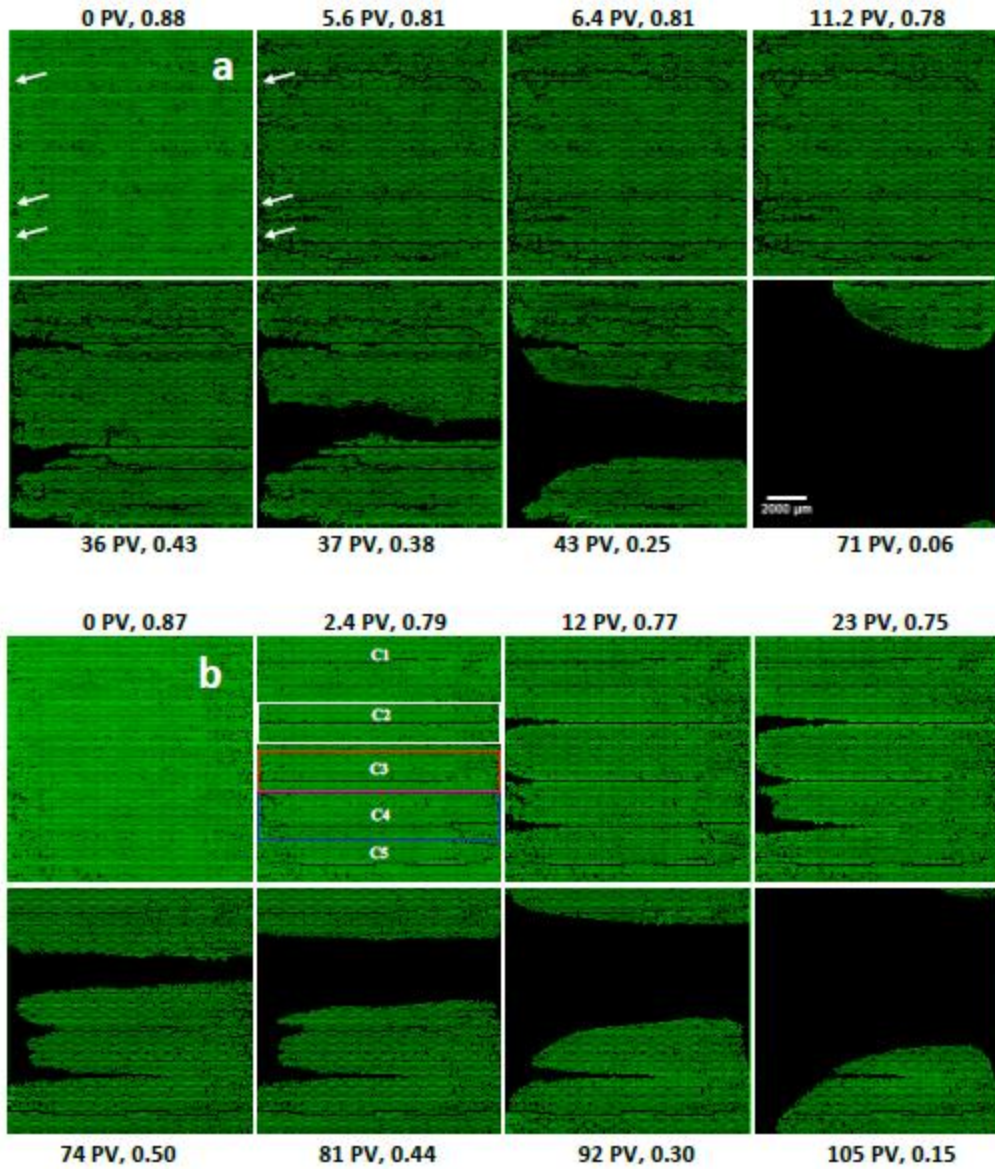
**Figure 1.** Pore characteristics of the four micromodels used in this study, with silicon posts in black and pore space in white. The sandstone-analog Micromodel #4 consists of nine identical sub images in a  $3 \times 3$  array, marked by the red dash lines. The blue arrow indicates the water flow direction during imbibition and dissolution experiments. The magnified images for Micromodel #2 and #3 are not to scale.



**Figure 1**

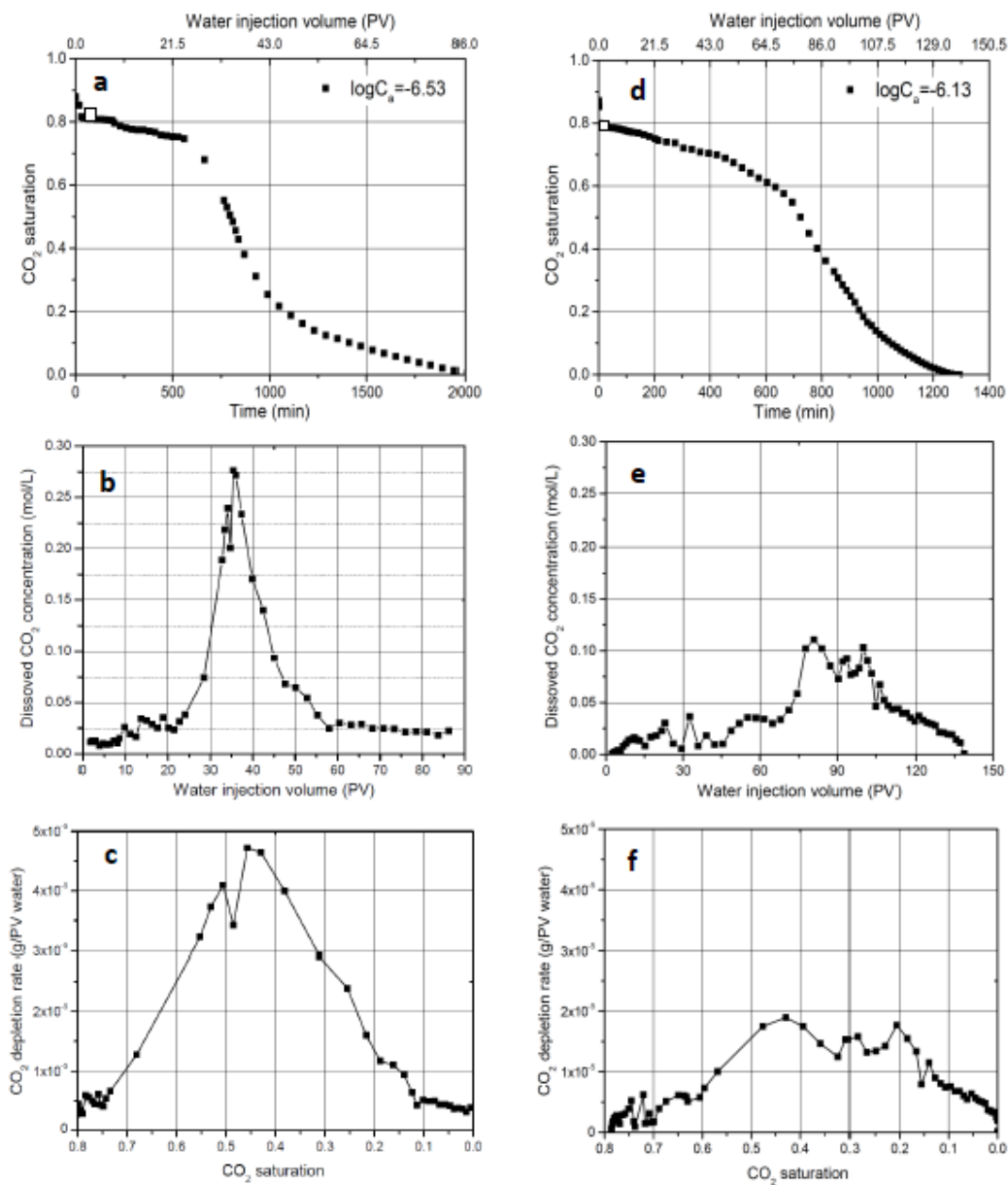


**Figure 2.** Time-lapse images of scCO<sub>2</sub> phase (green) at different times for water imbibition experiments at  $\log C_a = -6.53$  (a) and  $-6.13$  (b) in Micromodel #1. Water flow is from left to right. The white arrows in (a) indicate the water clusters distributed near the inlet before and after water injection. C1-C5 in (b) marks the five water flow paths developed after imbibition. The white, red and blue boxes indicate the regions magnified to show the competitions between flow paths in Figure 6.



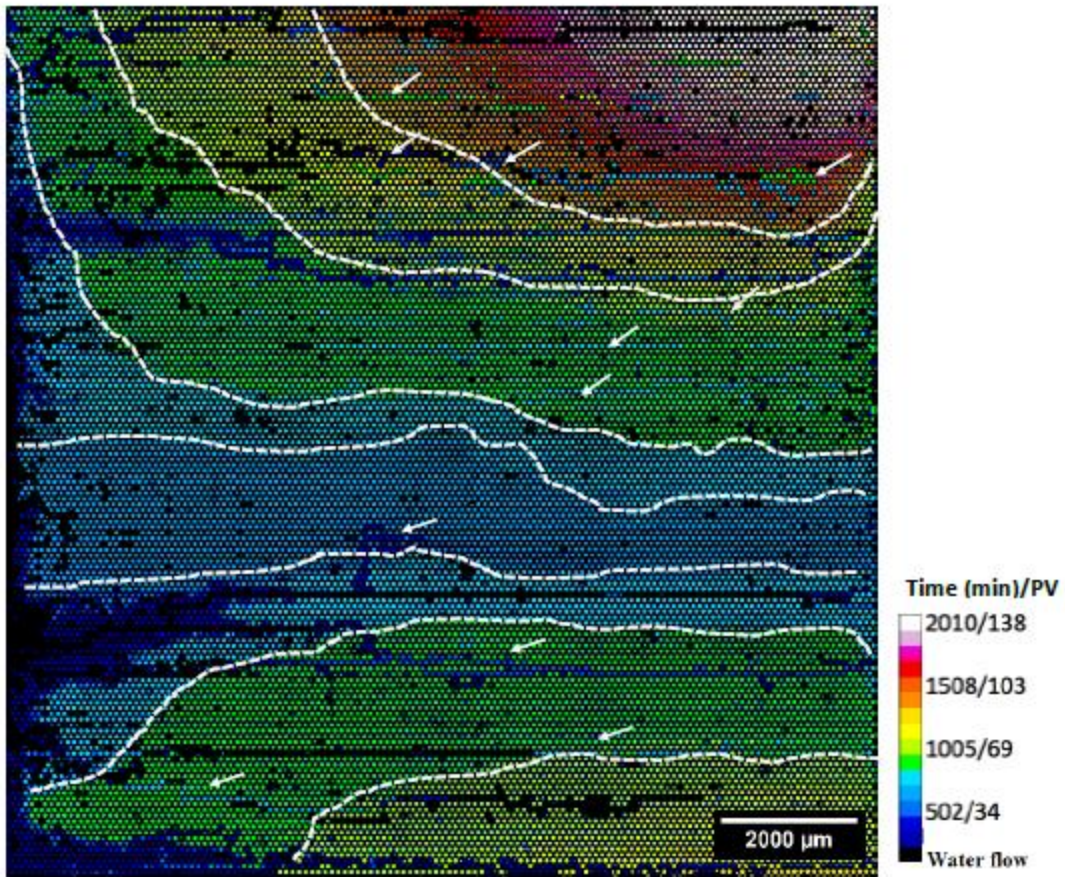
**Figure 2**

**Figure 3.** Temporal change in CO<sub>2</sub> saturation, dsCO<sub>2</sub> concentration vs. water injection volume and CO<sub>2</sub> depletion rate vs. CO<sub>2</sub> saturation for imbibition and dissolution experiments at  $\log C_a = -6.53$  (a-c) and  $\log C_a = -6.13$  (d-f) in Micromodel #1. The hollow symbols in (a) and (d) indicate the data points at residual CO<sub>2</sub> saturation.



**Figure 3**

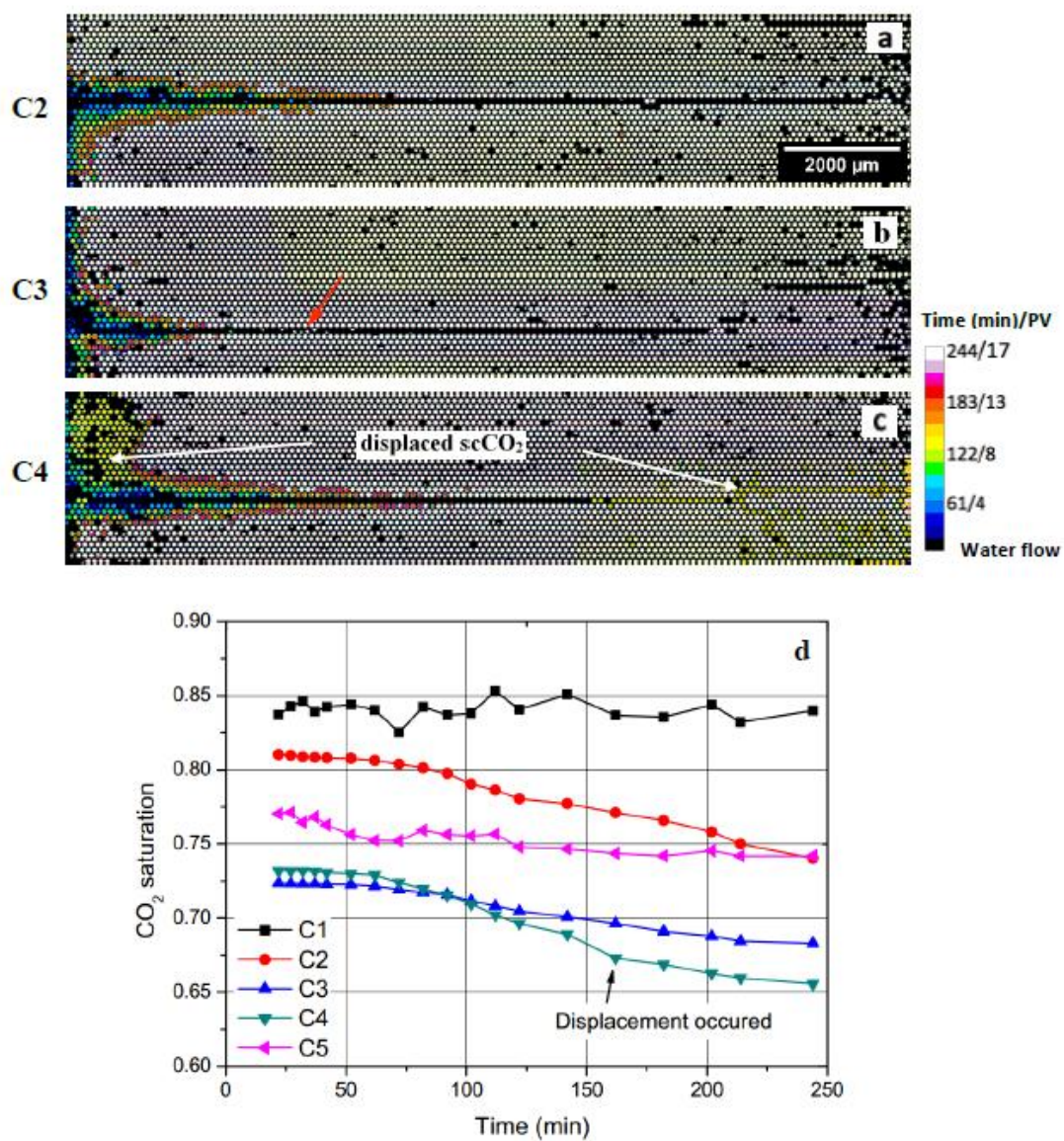
**Figure 4.** Dynamic dissolution and depletion of the residual  $\text{scCO}_2$  at different time intervals and water injection volumes (PV), marked by different colors, during imbibition and dissolution experiments at  $\log C_a = -6.53$  in Micromodel #1. Water flow paths developed during imbibition are shown in black. The white dotted lines indicate the boundaries of the two large  $\text{scCO}_2$  clusters at different times. The white arrows indicate the newly created water flow paths at localities.



**Figure 4**

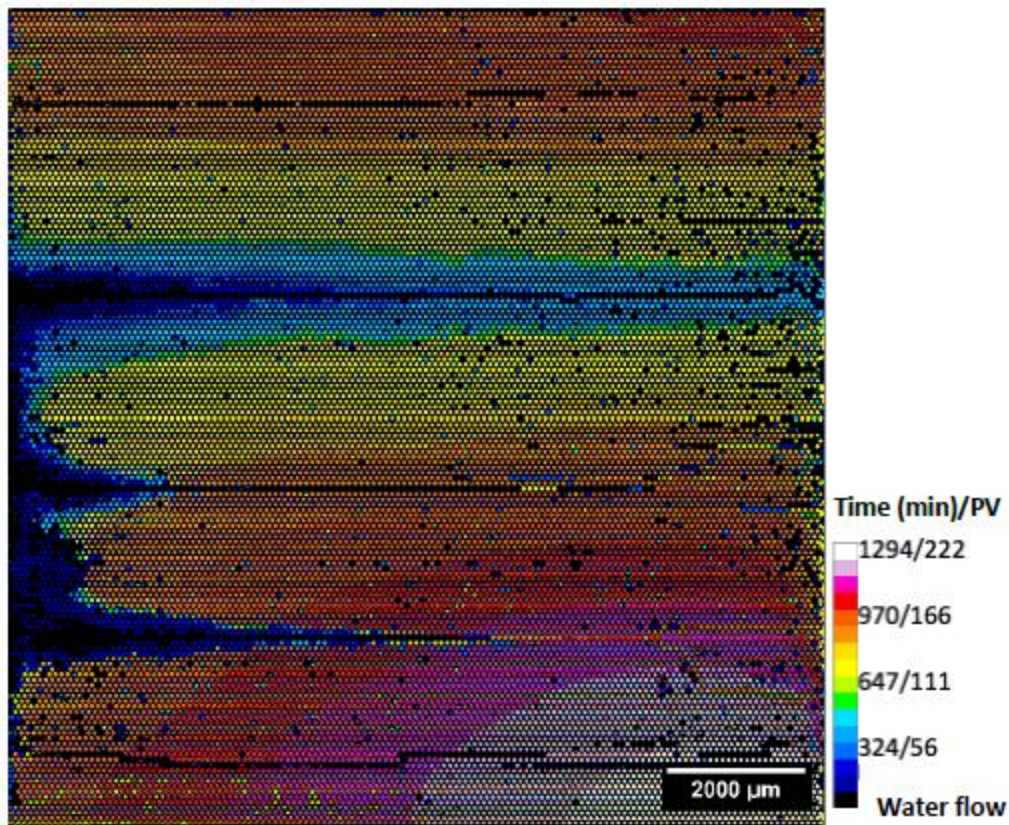
**Figure 5.** Magnified local regions (with ~30 pores wide) showing the dissolution and depletion of residual scCO<sub>2</sub> along the water flow paths #C2 (a), #C3 (b) and #C4 (c) at different time intervals and water injection volumes (PV) marked by different colors, during the imbibition and dissolution experiment at  $\log C_a = -6.13$  in Micromodel #1. (d) Relationship of CO<sub>2</sub> saturation vs. time along the five water flow paths at ~30 pore width regions. The red arrow in (b) points to the stable scCO<sub>2</sub> bubbles within the narrow flow path and the white arrows in (c) point to the displaced scCO<sub>2</sub> cluster (in yellow) within flow path #C4.





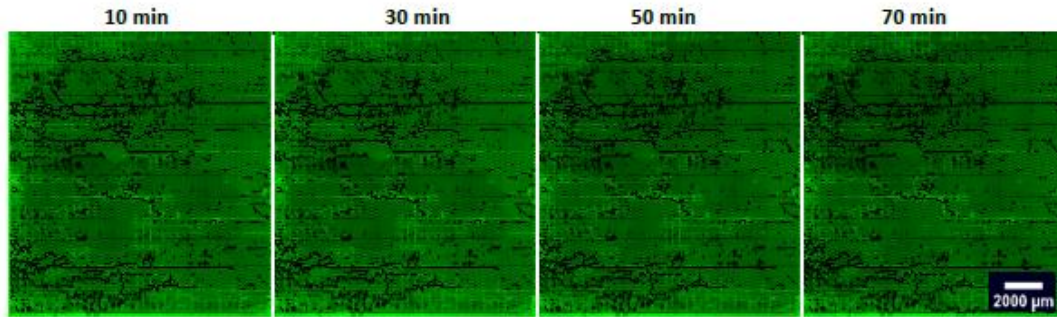
**Figure 5**

**Figure 6.** Dynamic dissolution and depletion of residual  $\text{scCO}_2$  at different time intervals and water injection volumes (PV), marked by different colors, during imbibition and dissolution experiment at  $\log C_a = -6.13$  in Micromodel #1. Water flow paths developed during imbibition are shown in black.



**Figure 6**

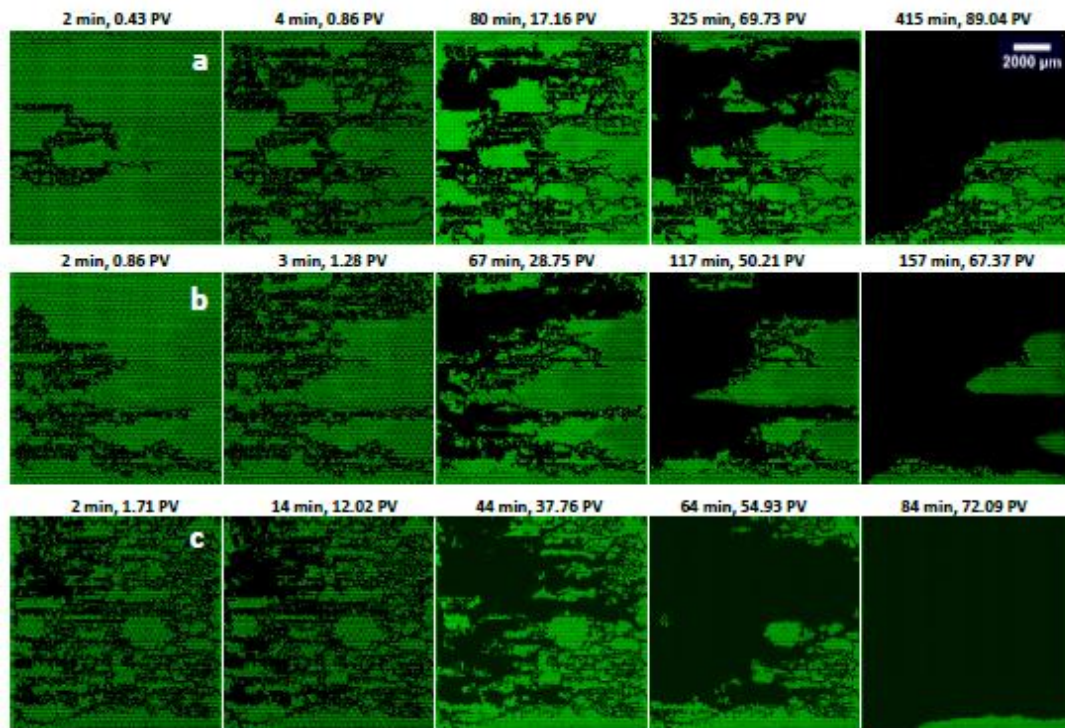
**Figure 7.** Time-lapse images of scCO<sub>2</sub> phase (green) at different times during imbibition with CO<sub>2</sub>-saturated water at  $\log C_a = -6.13$  in Micromodel #1. Water flow is from left to right.



**Figure 7**

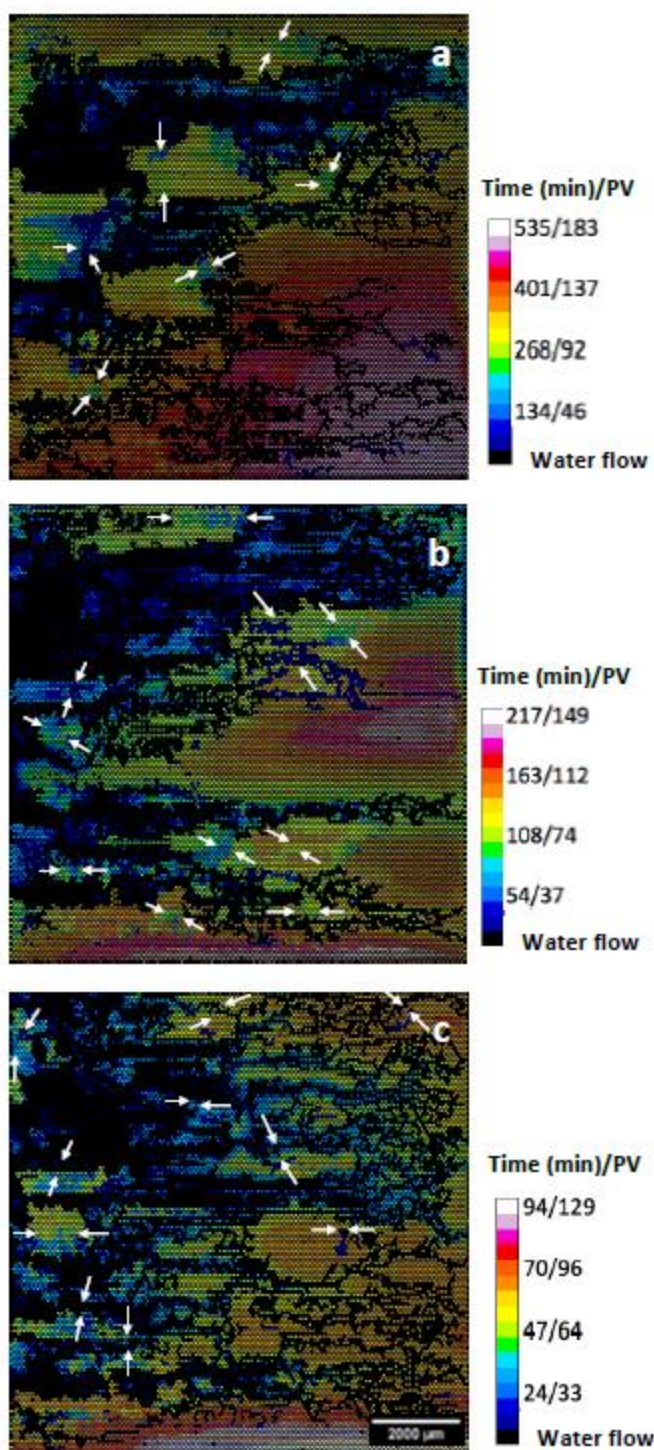


**Figure 8.** Time-lapse images of scCO<sub>2</sub> phase (green) at different times for imbibition and dissolution experiments in Micromodel #1 at (a)  $\log C_a = -5.83$  (b)  $\log C_a = -5.53$  and (c)  $\log C_a = -5.23$ . Water flow is from left to right.



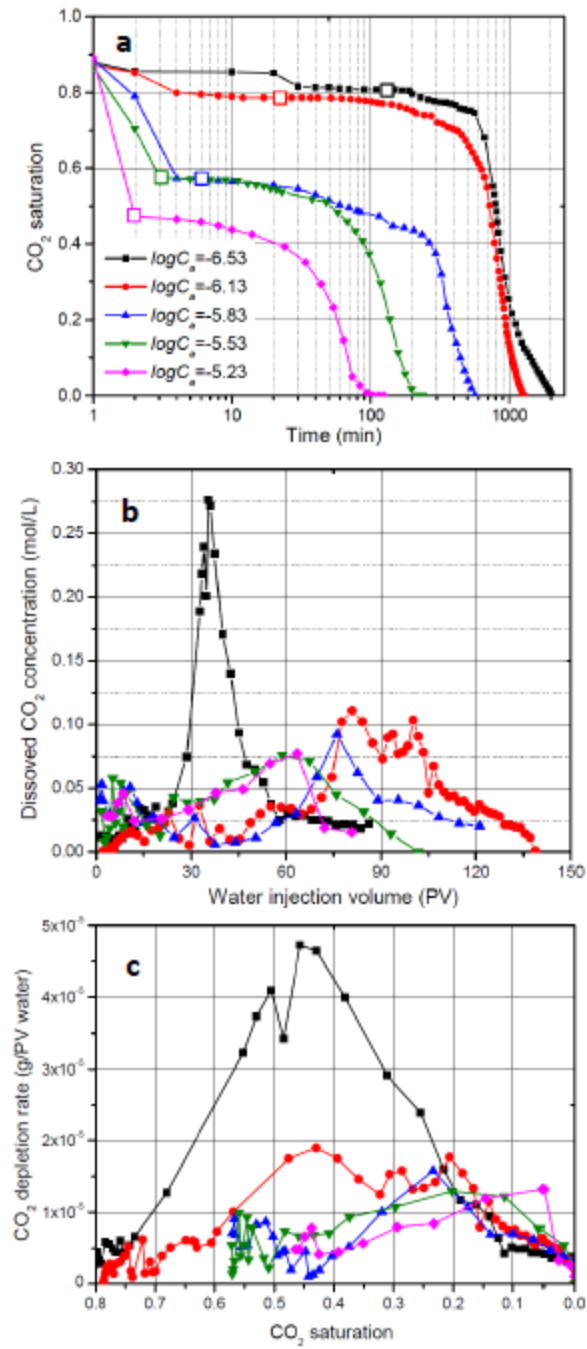
**Figure 8**

**Figure 9.** Dynamic dissolution and depletion of the residual  $\text{scCO}_2$  at different time intervals and water injection volumes (PV) marked by different colors, during imbibition and dissolution experiments at  $\log C_a = -5.83$  (a),  $-5.53$  (b) and  $-5.23$  (c) in Micromodel #1. Water flow paths developed during imbibition are shown in black. The white arrows indicate the newly created water flow paths.



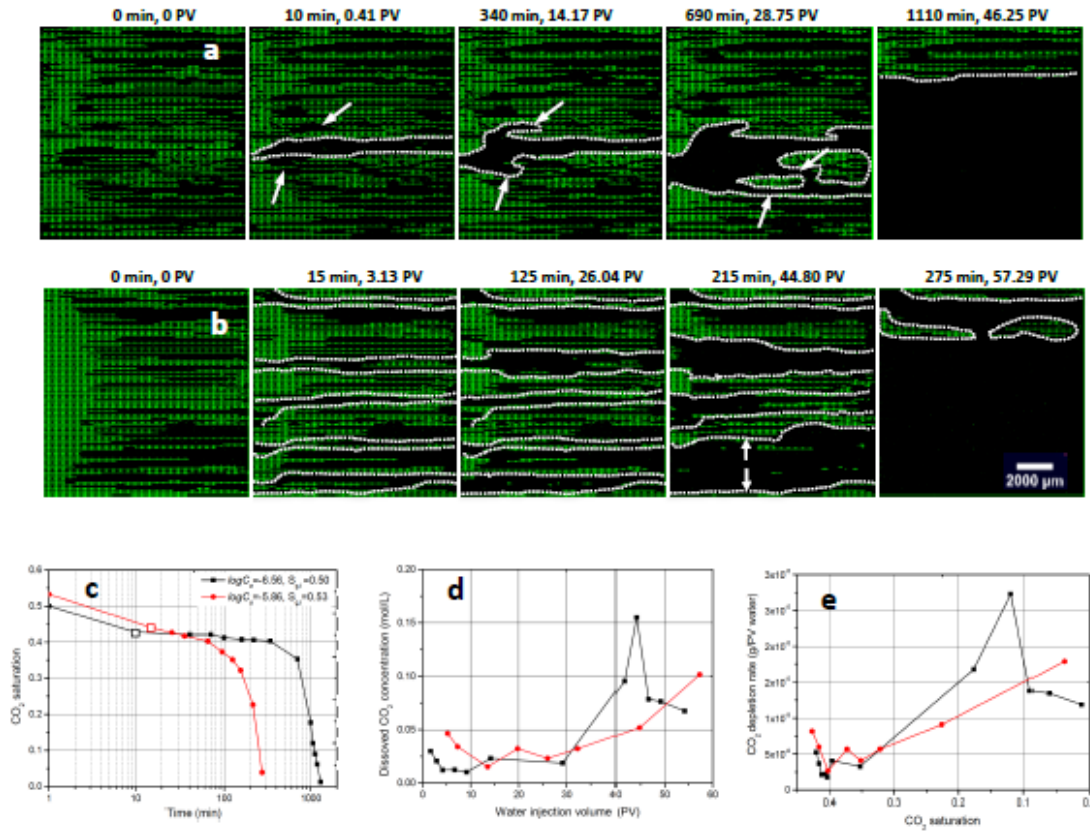
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**Figure 10**

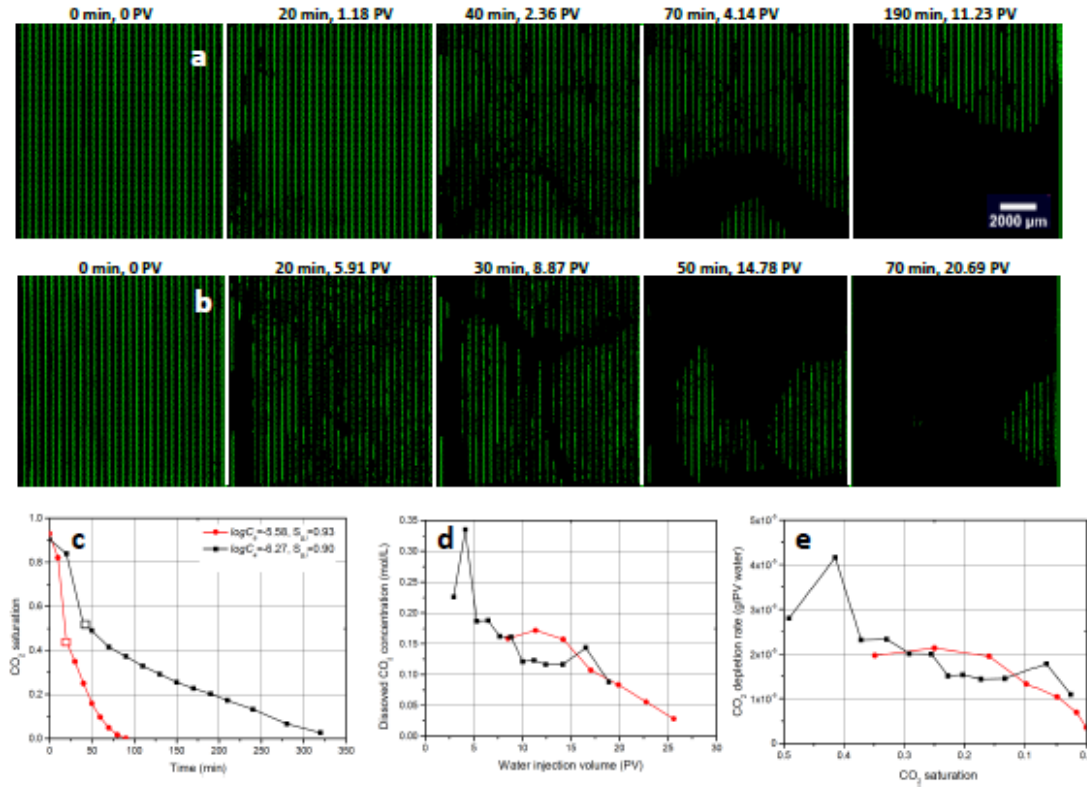
**Figure 11.** Time-lapse images of scCO<sub>2</sub> phase (green) at different times for imbibition and dissolution experiments conducted in Micromodel #2 at  $\log C_a = -6.56$  (a) and  $\log C_a = -5.86$  (b). Water flow is from left to right. The associated temporal change in CO<sub>2</sub> saturation, dsCO<sub>2</sub> concentration vs. water injection volume, and CO<sub>2</sub> depletion rate vs. CO<sub>2</sub> saturation are shown in (c)-(e), respectively. The white dotted lines in (a) and (b) show boundaries of water-flow paths and scCO<sub>2</sub>-filled clusters. The white arrows indicate the merger of displacing water with residual water clusters in (a) and several flow paths merge into a larger one in (b) as scCO<sub>2</sub> dissolved.



**Figure 11**

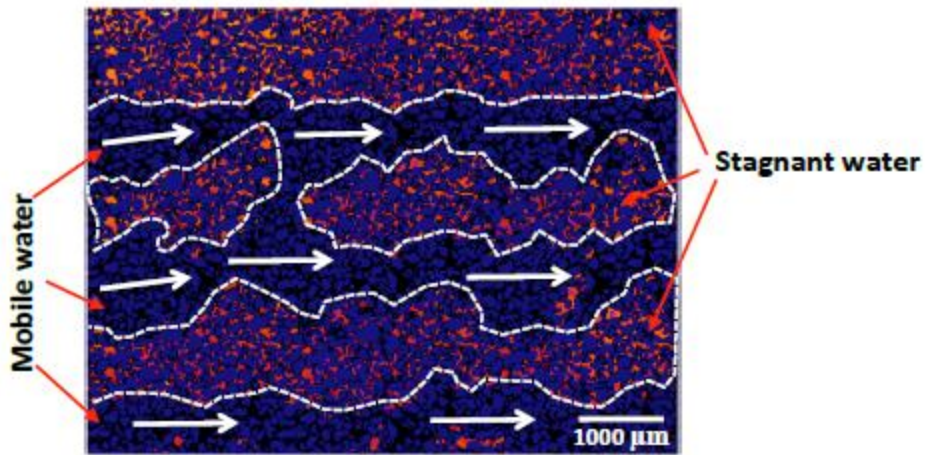


**Figure 12.** Time-lapse images of scCO<sub>2</sub> phase (green) at different times for imbibition and dissolution experiments in Micromodel #3 at  $\log C_a = -6.27$  (a) and  $-5.58$  (b). Water flow is from left to right. The associated temporal change in CO<sub>2</sub> saturation, dsCO<sub>2</sub> concentration vs. water injection volume, and CO<sub>2</sub> depletion rate vs. CO<sub>2</sub> saturation are shown in (c)-(e), respectively. The hollow symbols in (c) indicate the data points at residual CO<sub>2</sub> saturation.



**Figure 12**

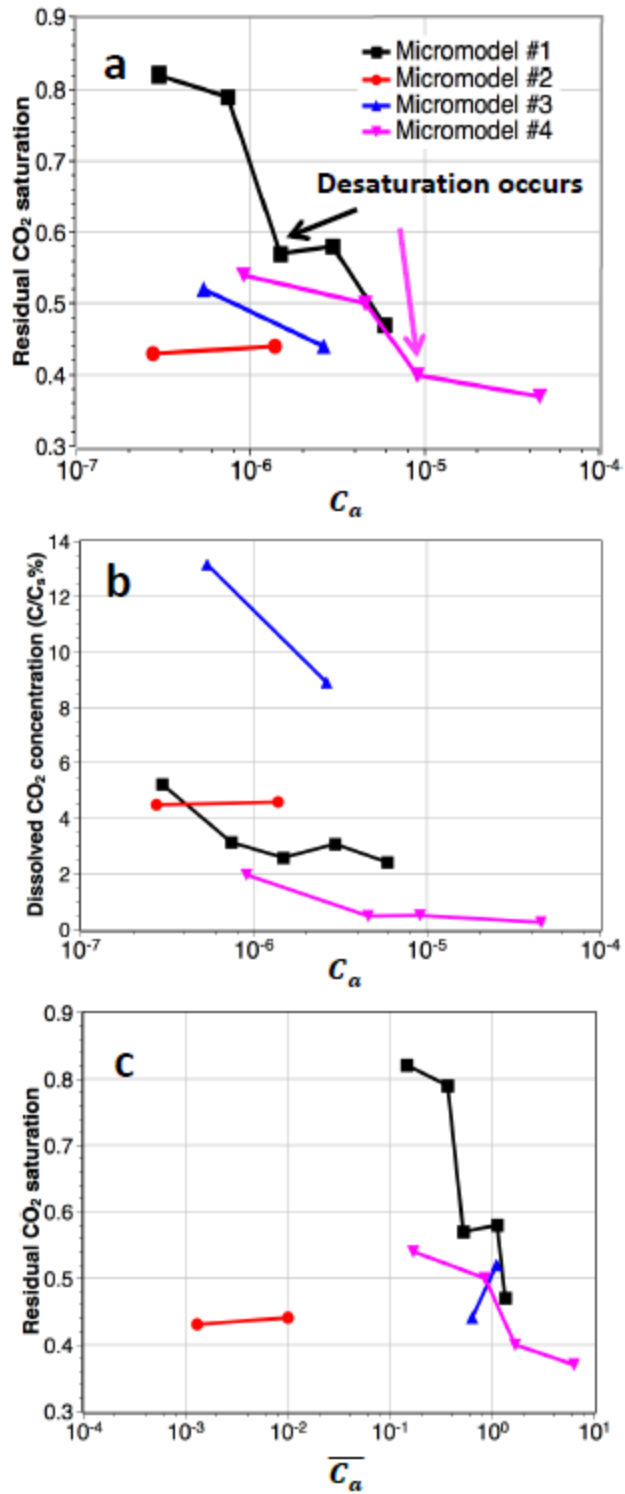
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**Figure 13**

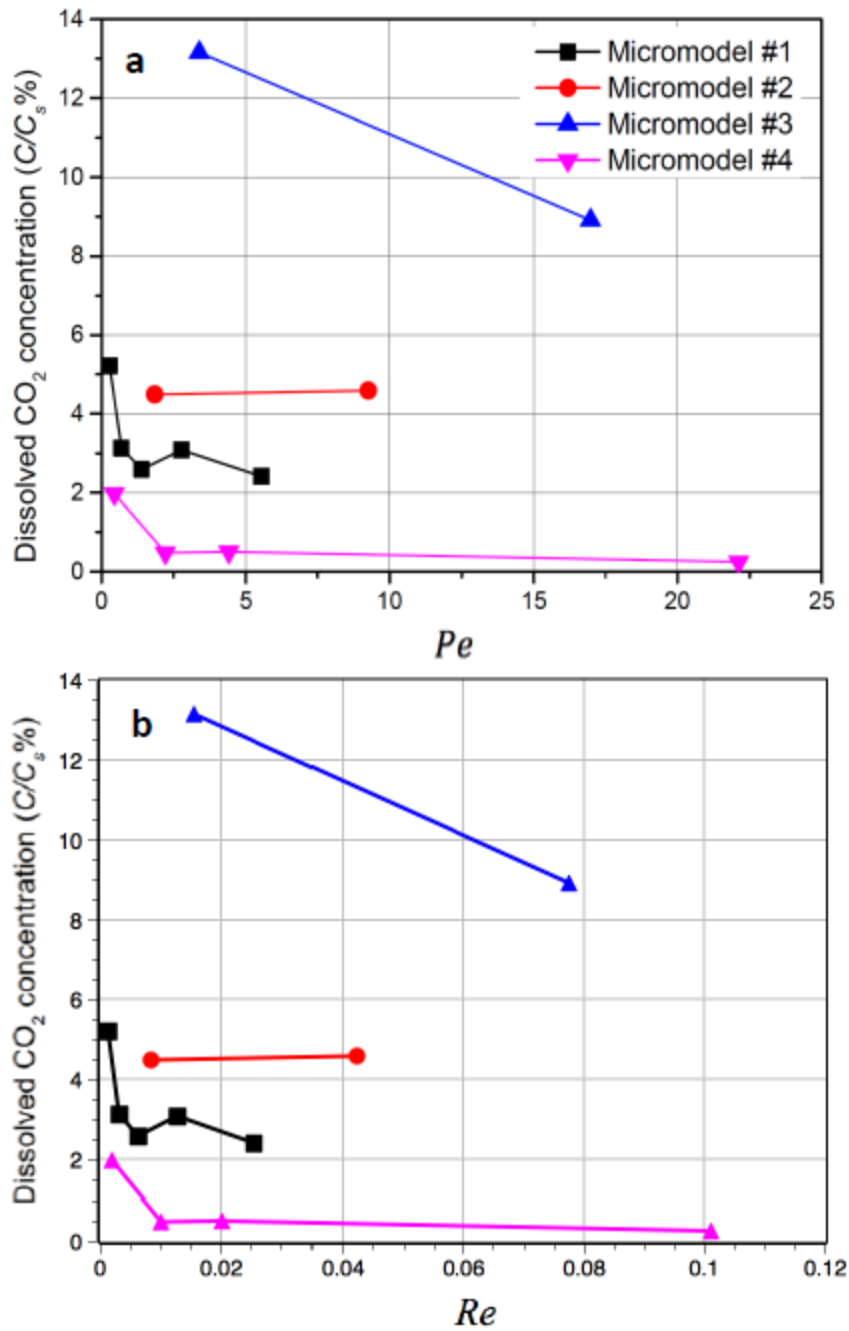


Figure 14. (a) Residual  $\text{CO}_2$  saturation and (b) dissolved  $\text{CO}_2$  concentration vs. capillary number  $C_a$  for the imbibition and dissolution experiments conducted in the four micromodels. (c) Residual  $\text{CO}_2$  saturation vs. the cluster-based capillary number  $\overline{C_a}$  in each experiment.



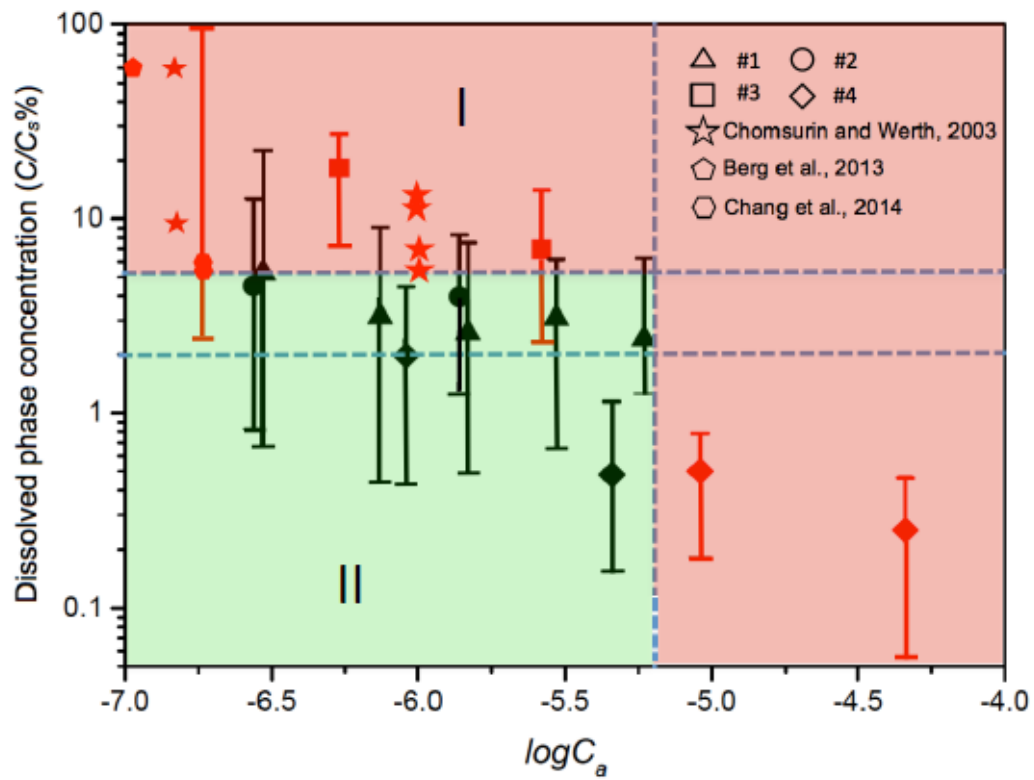
**Figure 14**

**Figure 15.** Dissolved  $\text{CO}_2$  concentration as a function of (a) Peclet number  $Pe$  and (b) Reynold number  $Re$  for the imbibition and dissolution experiments conducted in the four micromodels.



**Figure 15**

**Figure 16.** Dissolved phase concentration vs.  $\log C_a$  for the imbibition and dissolution experiments conducted in the four micromodels in this study, and in two different micromodels by Chomsurin and Werth (2003), in rock cores by Berg et al. (2013) and Chang et al. (2014). The red color bars indicate experiments where the dissolved phase concentration decreased monotonically with decreasing residual phase saturation. The black color bars indicate experiments where non-monotonic change was observed for the dissolved phase concentration vs. residual saturation, when coupled CO<sub>2</sub> dissolution and water flow occur. Zones I (in red) and II (in green) are partitioned by the horizontal dashed line at a relative concentration of 5% and a vertical one at  $\log C_a$  of  $-5.20$ . The horizontal dashed line at a relative concentration of 2% separates the relative concentration in the heterogeneous micromodel from the other micromodels and cores.



**Figure 16**

Table 1 Micromodel Properties

<b>Micromodel</b>	<b>#1</b>	<b>#2</b>	<b>#3</b>	<b>#4</b>
<b>Length×Width (cm×cm)</b>	1.2×1.2	1.2×1.2	1.2×1.2	0.71×0.53
<b>Depth (μm)</b>	37	37	37	35
<b>Porosity</b>	0.44	0.47	0.25	0.35
<b>Permeability (m<sup>2</sup>)</b>	6.3×10 <sup>-13</sup>	2.9×10 <sup>-11</sup>	1.1×10 <sup>-13</sup>	7.4×10 <sup>-13</sup>

Table 2 Summary of the imbibition and dissolution experiments conducted in different pore networks

	$S_{g,i}$	$Q$ ( $\mu\text{L/h}$ )	$\bar{u}$ (m/d)	$\log C_a$	$Re \times 100$	$Pe$
#1	0.88	10	1.2	-6.53	0.13	0.28
	0.87	25	3.0	-6.13	0.32	0.69
	0.89	50	6.0	-5.83	0.63	1.39
	0.87	100	12.0	-5.53	1.27	2.78
	0.89	200	24.0	-5.23	2.54	5.56
#2	0.50	10	1.2	-6.56	0.85	1.85
	0.53	50	6.0	-5.86	4.23	9.26
#3	0.90	10	2.2	-6.27	1.55	3.40
	0.93	50	11.0	-5.58	7.76	17.00
#4	0.70	10	3.7	-6.04	0.20	0.44
	0.72	50	18.5	-5.34	1.00	2.21
	0.68	100	37.0	-5.04	2.02	4.43
	0.71	500	185.0	-4.34	10.10	22.13

Note:  $Re = \rho \bar{u} L / \mu$ ,  $Pe = \bar{u} L / D$ , where  $\rho$  is water density. The characteristic length scale ( $L$ ) equals to the median pore diameter (Chomsurin and Werth, 2003). For micromodel #1 to #4,  $L_1=60 \mu\text{m}$ ,  $L_2=400 \mu\text{m}$ ,  $L_3=400 \mu\text{m}$ ,  $L_4=31 \mu\text{m}$  (Chang et al., 2017). The diffusion coefficient of  $\text{CO}_2$  in water ( $D$ ) was estimated as  $3 \times 10^{-9} \text{ m}^2/\text{s}$ , from Cadogan et al., (2014).

Table 3 Results of the imbibition and dissolution experiments in different pore networks

	$\log C_a$	$S_{g,r}$	Imbibition time (min)	Dissolution time (min)	$Q_d \times 10^7$ (g/min)	$C/C_s \times 10^2$	$l^{cl}(cm)$
#1	-6.53	0.82	150	1860	4.69	5.22	1.20
	-6.13	0.79	22	1272	7.04	3.13	1.20
	-5.83	0.57	8	557	11.65	2.59	0.86
	-5.53	0.58	3	235	27.67	3.08	0.91
	-5.23	0.47	2	122	43.38	2.41	0.55
#2	-6.56	0.43	10	1290	4.03	4.49	0.41
	-5.86	0.44	15	260	20.64	4.59	0.63
#3	-6.27	0.52	40	280	11.82	13.16	1.00
	-5.58	0.44	20	70	40.0	8.91	0.12
#4	-6.04	0.54	10	750	1.77	1.97	0.71
	-5.34	0.50	10	575	2.14	0.48	0.71
	-5.04	0.40	10	220	4.48	0.50	0.71
	-4.34	0.37	1.0	70	11.43	0.25	0.53